

Anionic Activation of CO₂ via (M_n-CO₂)⁻ Complex on Magic-Numbered Anionic Coinage Metal Clusters M_n⁻ (M = Cu, Ag, Au)

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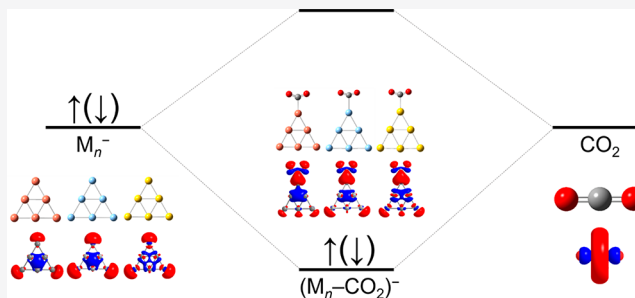


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ABSTRACT: Given the immense challenge of excessive accumulation of carbon dioxide (CO₂) in the earth's atmosphere, an extensive search is under way to convert atmospheric CO₂ to compounds of more utility. With CO₂ being thermodynamically extremely stable, activation of CO₂ is the first and most important step toward its chemical conversion. Building upon our earlier model for the anionic activation of CO₂ with azabenzene and inspired by the work of others on metal atom-CO₂ complexes, we investigated the possibility of anionic activation of CO₂ on small anionic metal clusters, which would have implications for catalytic conversion of CO₂ on metal surfaces with atomic-scale structural irregularities. We carried out theoretical calculations using density functional theory to examine small anionic metal clusters of Cu, Ag, and Au to check whether they form a complex with CO₂, with the sign of CO₂ being chemically activated. We found that a class of anionic metal clusters M_n⁻ with 1, 2, and 6 atoms consistently produced the activated complex (M_n-CO₂)⁻ for all three metals. There exists a strong interaction between the CO₂ moiety and M_n⁻ via a partially covalent M-C bond with a full delocalization of the electronic charge, as a result of electron transfer from the HOMO of M_n⁻ to the LUMO of CO₂ as in metal-CO₂ π-backbonding. We examined the interaction of frontier orbitals from the viewpoints of the orbital geometry and orbital energetics and found that the above magic numbers are consistent with both aspects.



INTRODUCTION

CO₂ is a major product of hydrocarbon combustion and a quintessential culprit in the greenhouse effect in earth's atmosphere. Although the neutral CO₂ molecule is extremely stable, its anionic form exists in a metastable state, which points to the possibility for chemical conversion of CO₂ to other useful compounds once it is anionically activated.¹ The CO₂⁻ anion has a lower bond order than neutral CO₂, hence weaker chemical bonds and a bent geometry,^{2,3} which lets the CO₂⁻ anion act as an activated doorway state on the way to chemical conversion.

In practice, anionic activation of CO₂ is difficult to achieve because CO₂ has a negative electron affinity^{2,3} and negative reduction potentials for most redox reactions.⁴ We found, however, that a certain chemical environment can place CO₂ in an anionically activated form. For example, the neutral van der Waals complexes between azabenzene and CO₂ turn into covalently bonded single-moiety adducts, with CO₂ in an anionically activated form, once an electron is added.^{5,6} Johnson and co-workers positively identified the covalent nature of the bond between pyridine and CO₂ in such an anionic complex.⁷

The anionic activation has been exploited in the conversion of CO₂ to methanol via pyridine-catalyzed electrochemical reduction.^{8,9} In this multielectron reaction initiated with the pyridinium accepting an electron from the electrode, the

formation of the pyridinium-CO₂ complex was identified as the first and rate-determining step.

Of particular interest is the fact that the pioneering studies by Weber and co-workers found that single metal atoms can also play a similar role in the anionic activation of CO₂ via (M-CO₂)⁻ complexes (M = Cu, Ag, Au).^{10–14} These coinage metals share many chemical properties because of their common valence electron configurations (d¹⁰s¹), but it is not straightforward to predict whether clusters of multiple metal atoms maintain the same catalytic function and which of them do so, which would have significant implications for catalytic reduction of CO₂ on metal surfaces with atomic-scale irregularities.

In this paper, we report that only a small subset of coinage metal clusters sharing a common set of “magic numbers” are effective toward anionic activation of CO₂ and show that such characteristics result from orbital interactions between the HOMO of M_n⁻ and the LUMO of CO₂.

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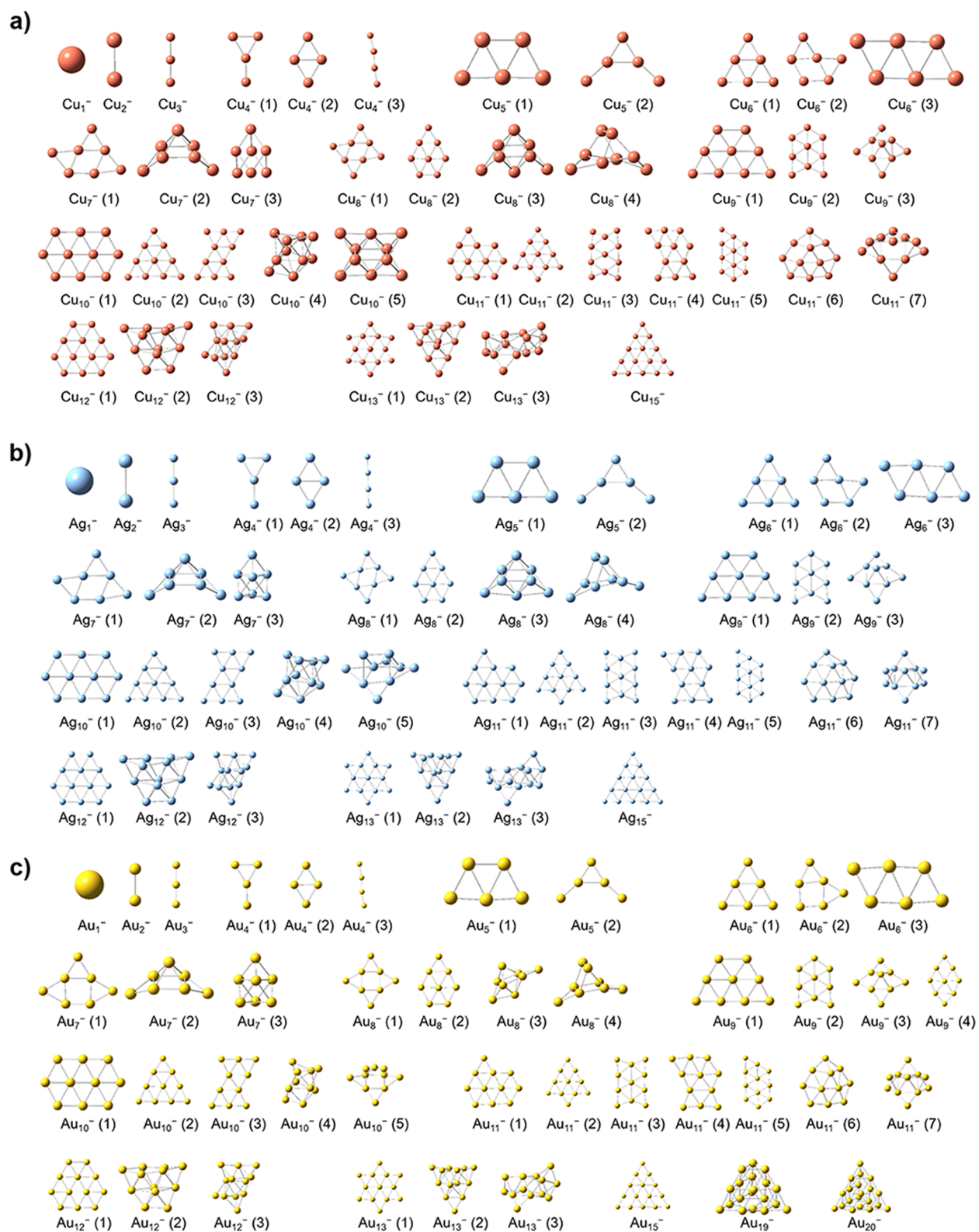


Figure 1. Optimized geometries of anionic (a) copper, (b) silver, and (c) gold clusters calculated by B3LYP/LANL2DZ. The number in parentheses is the label of a given isomer of the cluster species.

■ COMPUTATIONAL METHODS

We carried out density functional theory (DFT) calculations using the Gaussian 09 package (revision D.01)¹⁵ with the B3LYP,¹⁶ B971,¹⁷ BP86,^{18,19} PBEPBE,²⁰ and PW91PW91^{21,22} exchange–correlation functionals. All calculations were per-

formed without symmetry constraints. The LANL2DZ^{23–25} basis set with effective core potential was used for Cu, Ag, and Au, and the 6-311++g(3df,3pd) basis set was used for C and O. Atomic charges were obtained by Mulliken population analysis.

To investigate the $(M_n-\text{CO}_2)^-$ complexes, the geometry of the M_n^- clusters was optimized first, which yielded structures most akin to those found in earlier studies for anionic gold clusters.^{26–28} Our results are shown in Figure 1 for expedient reference here. Then, various initial geometries were tried by placing a bent CO_2 molecule near each atom of every M_n^- cluster that exists in diverse structures, which were followed by optimization to obtain a stable geometry for the $(M_n-\text{CO}_2)^-$ complexes. The CO_2 that did not form a covalent bond with the M_n^- clusters drifted away during the optimization, while slowly unfolding into a linear structure.

RESULTS AND DISCUSSION

The most telltale sign for anionic activation of CO_2 would be a highly bent geometry of the CO_2 moiety in the $(M_n-\text{CO}_2)^-$ complexes. Before we explore such species, we made a complete mapping for the geometries of neat anionic metal clusters M_n^- ($1 \leq n \leq 20$) by using the density functional theory (DFT) with the B3LYP exchange–correlation functionals (see the [Supporting Information](#) for details). The results shown in Figure 1 are in general agreement with those reported earlier,^{29,30} including the celebrated Au_{20}^- cluster.³¹ There is little elemental dependency in these structures, suggesting that their efficacy toward anionic activation of CO_2 , if any, may also turn out to be so.

We then examined how these neat anionic metal clusters interact with CO_2 . Although most of these anionic clusters interact with CO_2 by a weak intermolecular force, only a small subset of them exhibit a stronger covalent interaction featuring a significantly shorter M–C bond length (2–2.5 Å, Table S1) and a strongly bent O–C–O angle (140–150°, Table S2 and Figure 2).

From our extensive DFT calculations for $(M_n-\text{CO}_2)^-$ ($1 \leq n \leq 20$) using 5 functionals (B3LYP, B971, BP86, PBEPBE, and PW91PW91), we found that only three magic numbers $n = 1, 2,$ and 6 lead to the activated form of CO_2 for all 3 metals Cu, Ag, and Au with all 5 functionals (Table S3). Their structures were nearly identical, regardless of the metal (Figure 2). Interestingly,

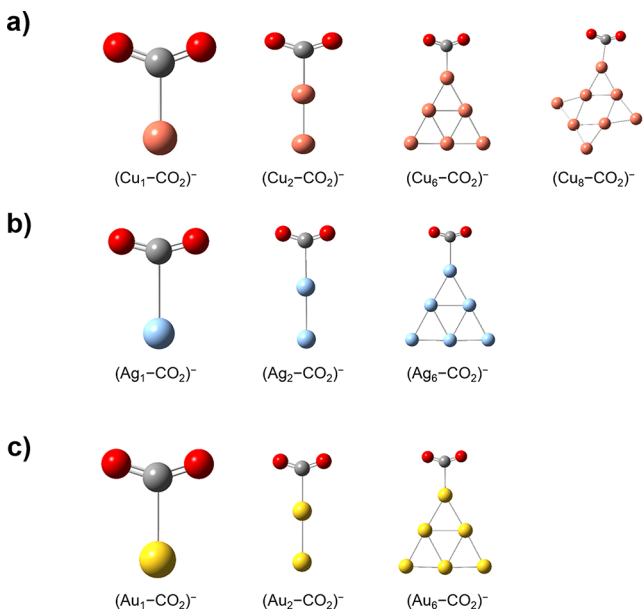


Figure 2. Optimized geometries for anionically activated CO_2 complexes with (a) copper, (b) silver, and (c) gold clusters calculated by B3LYP/6-311+g(3df,3pd)/LANL2DZ.

a fourth magic number, $n = 8$, was found for Cu with all 5 functionals and for Au with 3 functionals BP86, PBEPBE, and PW91PW9 (Table S3 and Figure S1).

Table S4 shows the calculated binding energy of the $(M_n-\text{CO}_2)^-$ complexes defined as $E_b = E[(M_n-\text{CO}_2)^-] - E[M_n^-] - E[\text{CO}_2]$, which reflects the relative stability of the complexes. The negative values indicate that these complexes are intrinsically more stable than the mere combination of their component species. Furthermore, the short bond length (2–2.5 Å, Table S1) between the carbon atom of CO_2 and its nearest metal atom confirms that the M–C bond in the $(M_n-\text{CO}_2)^-$ complexes is of partial covalent character, just as the N–C bond in the azabenzene– CO_2 anion complexes.^{5,6} The geometry of the CO_2 moiety may provide the clearest sign, with a strongly bent O–C–O angle (140–150°, Table S2) and a slightly elongated C–O bond (1.20–1.23 Å, Table S5), which more resemble the geometrical features of CO_2^- than those of CO_2 (two bottom entries of Tables S2 and S5). These geometrical features indicate that the anionic charge of the complex is considerably accommodated by the CO_2 moiety, despite the fact that CO_2 itself has a negative electron affinity (~ -0.6 eV).^{2,3}

A rudimentary examination of the electrostatic charge by Mulliken charge analysis for M_n^- and $(M_n-\text{CO}_2)^-$ showed that the CO_2 moiety in the complex is endowed with a considerable negative charge of -0.5 to $-0.8 e$ (Table S6 and Figures S2 and S3), which implies that the whole electronic charge is delocalized throughout the entire metal– CO_2 complexes, again as in the case of the azabenzene– CO_2 anion complexes.^{5,6} Interestingly, we found that the metal atom that ends up forming the M–C bond has its charge switched from negative to positive in Cu_6^- , Cu_8^- , Ag_6^- , and Au_6^- , but not in smaller clusters. Although the actual drain of electronic charge from the whole metal clusters to CO_2 is not as great as the change seen on this particular atom, it is notable that the charge drain is somewhat larger in larger complexes. The charge transfer from metal to CO_2 appears to mimic the π -backbonding that takes place between an adsorbate and a metal substrate.

We also note that all anionic complexes share the same structures and the same magic numbers, regardless of the metal (except for $n = 8$ with Cu). As there may exist a basic principle governing these common characteristics, we investigated the orbital structures for the HOMO of M_n^- clusters and the LUMO of CO_2 as well as the interaction between them. (In this work, we use “HOMO” to refer to both the HOMO and the SOMO, singly occupied molecular orbital, because some metal clusters have an odd number of electrons even in the neutral charge state.)

When an anion is formed by accepting an excess electron, the LUMO of the neutral molecule works as the frontier orbital and becomes the HOMO of the resulting anion, leading to the generic resemblance between the HOMO of the anion and the LUMO of the neutral molecule. All three coinage metals Cu, Ag, and Au share the same electronic configuration ($d^{10}s^1$), and thus the HOMOs of their anionic clusters are also quite alike, as shown in Figure 3 and more completely in Figure S4. Considering the shape of the LUMO of CO_2 (Figure 3b, top), we recognize that the “right” shape for the HOMOs of the anionic metal clusters to facilitate electron transfer to CO_2 is found in M_1^- , M_2^- , M_6^- , and M_8^- . The partially anionic CO_2^- moiety should have a HOMO that somewhat resembles the HOMO of fully anionic CO_2^- (Figure 3 b, bottom), whose combination with the HOMOs of the partially charged $M_n^{\delta-}$ would then yield the HOMOs of $(M_n-\text{CO}_2)^-$ shown in Figure

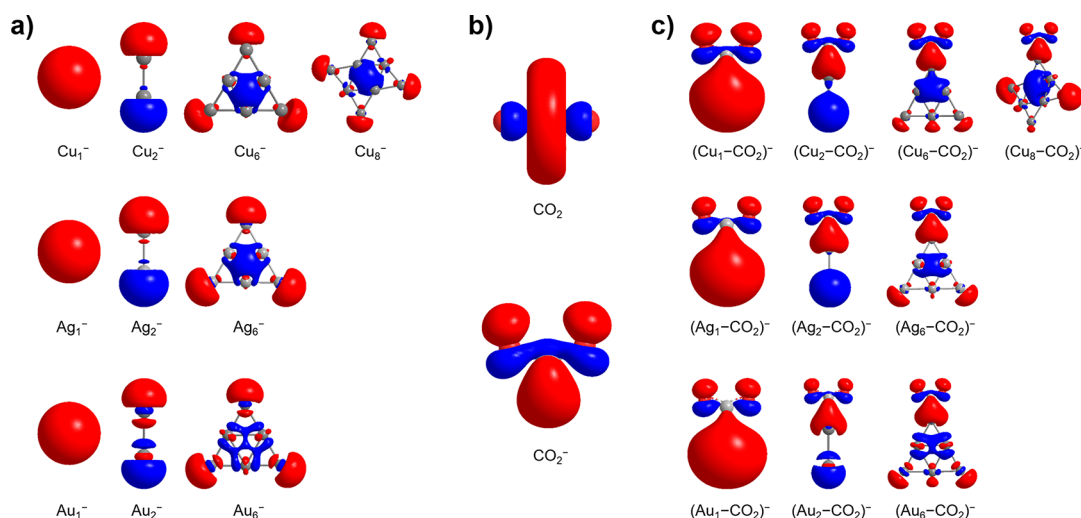


Figure 3. (a) HOMOs of M_n^- clusters, (b) LUMO of CO_2 (top) and HOMO of CO_2^- (bottom), and (c) HOMOs of $(M_n-\text{CO}_2)^-$ complexes calculated by B3LYP functional ($M = \text{Cu, Ag, Au}$; $n = 1, 2, 6$ (and 8 for Cu)).

3c. The (partial) covalency of the M–C bond and the charge delocalization over the entirety of the $(M_n-\text{CO}_2)^-$ adduct are the consequence of such orbital interaction, whose common characteristics are shared by all three metals.

The other crucial factor that governs orbital interaction, aside from the shapes of the frontier orbitals, is the energetics of the orbitals involved. When we consider the energetics of the frontier orbitals (*i.e.*, the HOMO of M_n^- and the LUMO of CO_2), we are reminded that CO_2 has a large HOMO–LUMO gap (of 9~10 eV), which places its LUMO only slightly below the vacuum level (Table S7). On the other hand, the HOMO levels of small anionic metal clusters M_n^- are also slightly below or above the vacuum level. (The fact that all of these anions are experimentally detectable indicates that the computational error is as large as ~2 eV in the case of B3LYP and B971 functionals and even higher with other functionals.) These high-lying HOMOs of small anionic metal clusters M_n^- would interact with the LUMO of CO_2 to form the HOMO of the adduct, $(M_n-\text{CO}_2)^-$ (Figure 4 a). In contrast, the HOMO levels of larger M_n^-

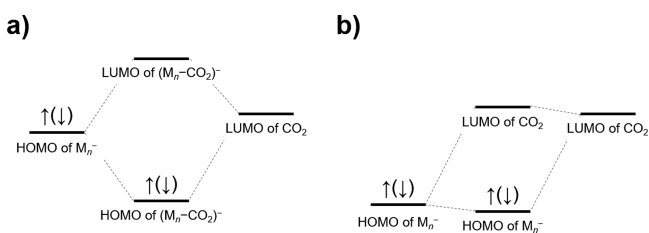


Figure 4. Schematic diagram for the molecular orbital interaction between CO_2 and (a) a smaller M_n^- cluster with a HOMO energy level roughly matching the LUMO level of CO_2 and (b) a larger M_n^- cluster with a lower HOMO energy level that does not significantly interact with the LUMO of CO_2 ($M = \text{Cu, Ag, Au}$).

clusters drop deeper in energy as the cluster size increases, which may be glimpsed from Table S8, leading to a larger energy gap with the LUMO of CO_2 (Figure 4 b) and a lower HOMO level of the anionic complex $(M_n-\text{CO}_2)^-$ (Table S9). As a result, the interaction between the HOMO of M_n^- and the LUMO of CO_2 becomes weaker as the cluster size increases, leading to a smaller binding energy (Table S4).

As explained above, the structural and energetic properties of HOMO are necessary conditions for the anionic coinage metal clusters to form an $\eta^1-\text{CO}_2$ complex. It is apparently important for M_n^- to have a frontier orbital with a proper shape, orientation, and symmetry. The requisite orientation and symmetry are rather obvious considering the C_2 symmetry of the LUMO of CO_2 (and the HOMO of CO_2^- as well), which excludes some M_n^- clusters with n other than 1, 2, and 6. For example, in the case of M_3^- , the orbital lobes on both ends have a severely truncated shape (like a doughnut) rather than a fully developed p-orbital-like one, as shown in Figure S5. Also, the interaction of frontier molecular orbitals is a major factor for the CO_2 activation because there is a clear commonality among CO_2 -binding clusters, but it is not an exclusively sufficient condition, as numerous other factors may come into the play.

Finally, we would like to make it clear that we found a range of diverse structures for $(\text{Cu}_n-\text{CO}_2)^-$ complexes in our cursory survey, which deviate from the canonical structures given in Figure 2. Whether these are significant structures with sufficient stability remains to be examined in detail by further studies. It is also possible that these noncanonical structures may reflect the unique tendency of Cu that often distinguishes itself from Ag and Au. For instance, we note that atoms with lower coordination numbers in M_n^- are more negatively charged than those with higher coordination numbers in the case of Ag and Au anion clusters (*i.e.*, Ag_6^- and Ag_8^- in Figure S2b and Au_6^- and Au_8^- in Figure S2c), which is consistent with the trend found in neutral Ag and Au clusters.³² In contrast, the opposite is true for Cu_6^- and Cu_8^- clusters (Figure S2a). The uniquely distinctive properties and reactivities of Cu are largely responsible for its wide-ranging applications in various photo-, electro-, and heterogeneous-catalysts for CO_2 conversion.^{33–35}

CONCLUSIONS

In summary, we found that anionic activation of CO_2 is possible on some small Cu, Ag, and Au clusters with the magic numbers of 1, 2, and 6 (and additionally 8 for Cu) atoms. The CO_2 moiety interacts strongly with the metal clusters via a partially covalent M–C bond with a full delocalization of the electronic charge, which leads to the formation of a single-moiety $(M_n-\text{CO}_2)^-$ complex. Electron transfer from the HOMO of M_n^- to the LUMO of CO_2 is believed to be at play, as in the metal– CO_2 π -

backbonding. We found that all of these $(M_n-CO_2)^-$ complexes share the same geometry, including two unmistakable geometrical signatures: a strongly bent O–C–O angle and elongated C–O bonds in the CO_2 moiety. We examined interaction of frontier orbitals from the viewpoints of the orbital geometry and orbital energetics and found that the magic numbers are consistent with both aspects.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.0c10867>.

HOMO structures of M_n^- clusters, and physical and chemical information about M_n^- and $(M_n-CO_2)^-$ clusters (binding energy, M–C distance, O–C–O angle, C–O distance, Mulliken charge, HOMO energy level, etc.) (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

DFT, density functional theory; HOMO, highest occupied molecular orbital; SOMO, singly occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

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